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AN INTERLABORATORY TEST FOR CERTIFICATION OF POTASSIUM CHLORIDE AS A CERTIFIED REFERENCE MATERIAL (CRM) FOR SOLUTION CALORIMETRY

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The enthalpy of solution of KCl in H_2O (1:2000 mol·mol^{-1}) at 298.15 K was measured in an interlaboratory test in the G.D.R. The test material was prepared in the ASMW laboratories. The purity found on the high-precision coulometric titration of chloride was 0.9999 ± 0.0001 g · g^{-1}. The consensus value of the enthalpy of solution in the test was $\Delta H_s^{298.15} = 17.47 \pm 0.07$ kJ·mol^{-1}. This result is in good agreement with experimental values from recognized international scientific laboratories. The test material is applicable as a CRM.

The enthalpy of solution of KCl in H_2O (1:2000 mol·mol^{-1}); $m = 0.02775$ mol kg^{-1}) at 298.15 K has been measured in an interlaboratory test organized by the ASMW in the GDR. This test was made (i) to show the ability of selected laboratories in the GDR to make accurate measurements, (ii) to produce in this way CRM KCl.

Experimental

Materials

The material for preparation of the KCl sample was a 10 kg charge commercial potassium chloride (p.a., purissimum, VEB Laborchemie Apolda, GDR; 99.8 mass per cent). It was purified in two steps in the chemical laboratories in the ASMW.

In the first step, KCl portions of 1 kg were dissolved in double-distilled water at 90°, and the solutions were filtered through a fritted glass filter. After this procedure, the KCl was precipitated through the dropwise addition of methanol and cooling at 20°. The precipitated KCl was separated, washed twice in methanol and dried for 4 h at 120°. In the second step, the whole charge was recrystallized from quartz-distilled water. To obtain a uniform particle size of 100–500 μm, the KCl solution was cooled according

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to a temperature programme, with a stirring device. After separation, the KCl was washed again and dried for 4 h at 150°. The yield of the overall procedure was 25 per cent of the starting material.

In the next operation, the KCl was sieved through standard bronze sieves. The fraction of 100–500 μm was taken and homogenized by shaking for 2 h in a glass container.

Test of purity

To test the purity, a high-precision coulometric titration of chloride was performed. To ensure lack of disturbance by bromide, a semi-quantitative colour test for bromide was carried out. A colour comparison with a series of calibration solutions showed that the bromide content in the starting material was lower than 0.01 mass per cent. The samples for the coulometric titration were taken from the homogenized final product and were treated in the same way as the samples for the interlaboratory test.

The titrations were carried out in a standard coulometric device built in the ASMW [1]. The determination of the purity was based on the determination of accurate measurable electrical quantities, time and mass, related by Faraday's law.

An attempt was made to minimize the relative systematic error of the device by calibration of the individual instruments in the ASMW. The relative systematic error of the whole device could be estimated as lower than 0.01 per cent.

The titration of chloride [2] was performed in a daylight-proof vessel with anodically produced silver ions in a special methanolic anolyte, with potentiometric determination of the end-point. The anode was pure silver with impurities lower than 5 ppm. The current density was 0.3 $A \cdot dm^{-2}$, and the sample mass averaged 0.2 g.

The results of 7 individual measurements were 1.00017, 0.99993, 0.99995, 0.99984, 1.00005, 0.99984 and 0.9997 $g \cdot g^{-1}$, with a mean of $\bar{x} = 0.99996 \pm 0.00011$ $g \cdot g^{-1}$ ($P = 0.95$).

The interlaboratory test

The concept of the certification of a CRM by an interlaboratory test was based on two assumptions:

1. there is a laboratory population in the GDR capable of determining CRM's with acceptable accuracy;
2. the differences between individual results, both within and between laboratories, are statistical in nature.

Each laboratory mean was considered to be an unbiased estimate of the characteristic of the material. The material was considered to be homogeneous after the homogenizing procedure and in view of the coulometric results. It was dried in a platinum vessel at 800 K for 8 h and cooled in a desiccator. Test portions in a dried nitrogen atmosphere in gas-proof glass vessels were prepared in ASMW laboratories and sent to the participants. The optimum drying conditons and particle size were obtained from the work of Kilday [3].

For the calorimetric measurements, the following conditions were fixed:

1. temperature: 298.15 K;
2. dilution: 1:2000 $mol \cdot mol^{-1}$ (KCl/H_2O) ($0.02775\ mol \cdot kg^{-1}$);
3. the measurements should be performed integrally with air-saturated double-distilled water;
4. each laboratory should carry out a minimum of 3 replicates.

The interlaboratory test was evaluated in the ASMW on the basis of the measurement reports, which contained all the individual results, estimations of systematic errors, technically explainable outliers, the measurement data, the names of the operators, and so on. This corresponds to the procedure recommended by the ISO [4].

Results

The results from all laboratories were tabulated systematically, and the technically explainable outliers were eliminated. Next, statistical outliers were looked for according to Dixon's r-test [5]. None were found. Laboratory means were calculated. No formation of clusters could be found in the individual laboratory results, and no correlation was observed between the date of measurement and the result. Table 1 shows the laboratory means and the standard deviations.

Table 1 – Results of the interlaboratory test (enthalpy of solution $\Delta H_s^{298.15\,\mathrm{K}}$, $m = 0.02775$ mol·kg^{-1})

Laboratory	Number of measurements	Sample mass, g	Type of calorimeter	Mean, kJ·mol^{-1}	Standard deviation, kJ·mol^{-1}
1	5	0.005	C 80	17.56	0.16
2	4	0.16	LKB 8700	17.37	0.02
3	4	0.15	NTK 82	17.37	0.16
4	27	0.19	NTK 82	17.55	0.10
5	8	0.21	LKB 8700	17.50	0.02
6	10	0.15	self-made	17.47	0.02
7	4	0.12	LKB 8700	17.47	0.17

In order to calculate a consensus value (mean of means), each laboratory mean was considered as an individual result and was taken as unbalanced. The consensus value was:
$\bar{\bar{x}} = 17.47 \pm 0.07$ kJ·mol^{-1} ($P = 0.95$).

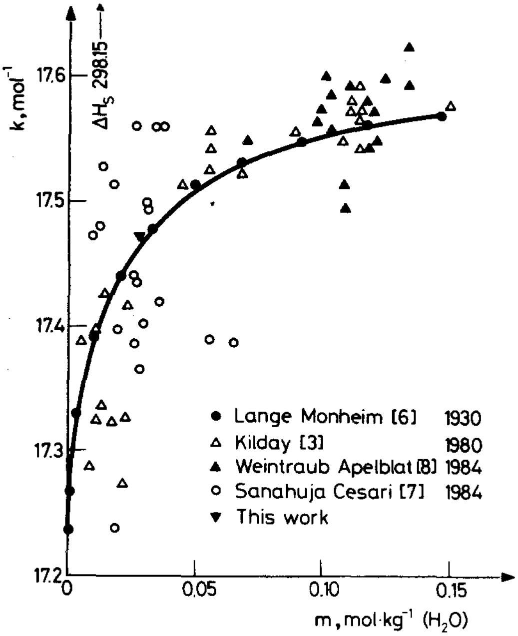

Fig. 1 Enthalpy of solution

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Discussion

Figure 1 shows experimental values from international scientific laboratories [6–8]. Our result is in good agreeement with these. The deviations between the laboratory means are acceptable too. In 1987, the IUPAC recommended a value of the enthalpy of solution [9] of $\Delta H_s^{298.15} = 17.59\pm$ ± 0.01 kJ·mol^{-1} for the dissolution KCL(cr) + 500 H_2O (1)= KCL 500 H_2O) (1).

We converted this value with Parker's tables [10] to a dilution of 1:2000 mol·mol^{-1}, and obtained $\Delta H_s = 17.49$ kJ·mol^{-1}. This result too is in good agreement with our value.

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Zusammenfassung – Die Lösungsenthalpie von KCl in Wasser (Molverhältnis 1:2000) bei 298.15 K wurde in einem Vergleichstest in mehreren Laboratorien der DDR gemessen. Das Testmaterial wurde in den Laboratorien des ASMW hergestellt. Eine coulometrische Präzisionstitration des Chlorids ergab seine Reinheit zu (0.9999 ± 0.0001 g/g. Der übereinstimmende Wert für die Lösungsenthalpie wurde in dem Test zu $\Delta H_s^{298.15} = (17.47 \pm 0.07)$ kJ mol^{-1} gefunden, in guter Übereinstimmung mit experimentellen Angabe aus internationalen Laboratorien. Nach Abschluss des Testes ist das Material als bestätigter Bezugsstandard verwendbar.

РЕЗЮМЕ — В ГДР было проведено измерение энтальпии растворения хлорида калия в 2000 моль/моль H_2O при температуре 298.75 К. С этой целью были проведены международные лабораторные испытания. Испытываемый материал был получен в лабораториях ASMW. Чистота материала, определенная высокоточным кулонометрическим титрованием хлорид-иона, составляла 0.9999 ± 0.0001 г·г$^{-1}$. Значение энтальпии растворения, полученное таким тестовым методом, составляла $\Delta H_S^{298.15} = 17.47 \pm 0.01$ кдж·моль$^{-1}$, что хорошо согласуется с экспериментальными значениями, найденными в других международных научных лабораториях. После окончания испытания, вещество было применено как CRM.